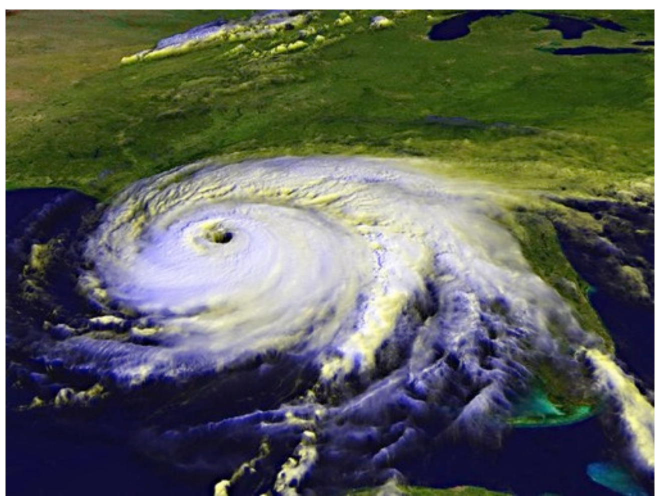
Exceptional service in the national interest

Sandia National Laboratories

energy.sandia.gov



Adv. Materials for Ionic Liquid Flow Battery

Thursday, September 24, 2015

Harry Pratt, Cy Fujimoto, Leo Small, Travis Anderson

U.S. DEPARTMENT OF ENERGY

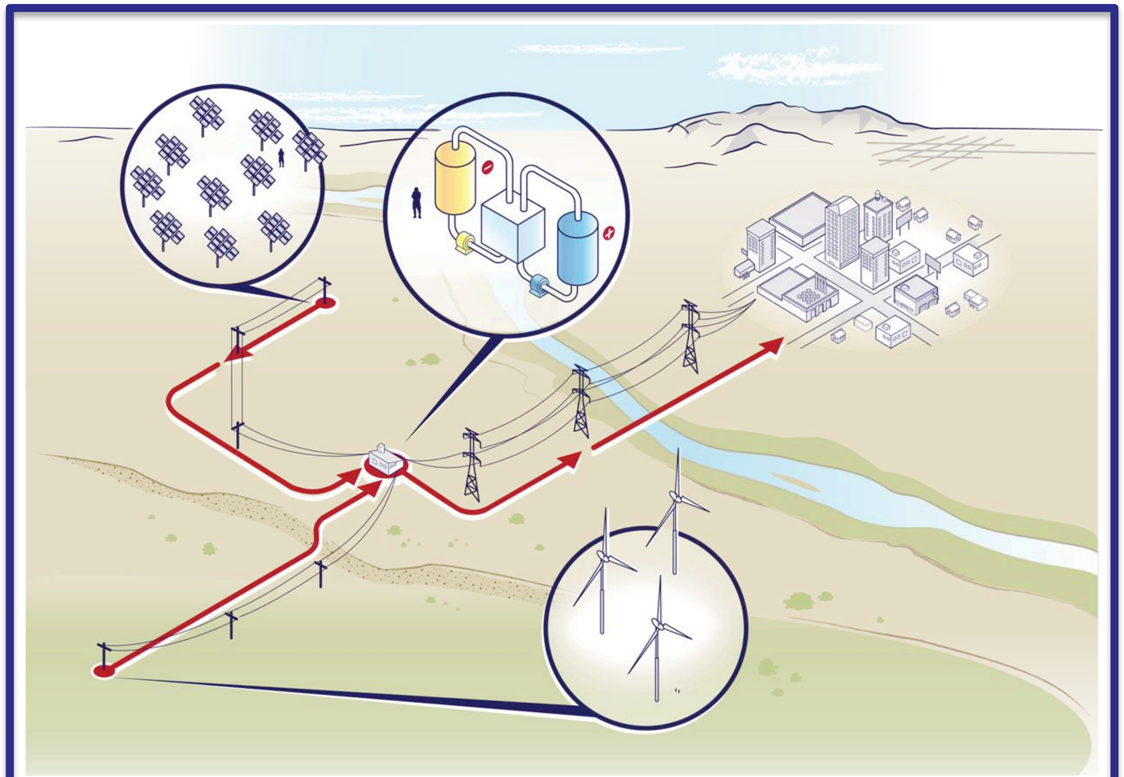
NNSA National Nuclear Security Administration

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000

Project Overview

Problem: Cost competitive ionic liquids have high viscosities but are promising for higher energy density redox flow batteries due to higher metal concentrations and wider voltage windows.

Approach: Couple earth-abundant, tunable electrolytes with custom-synthesis non-aqueous membranes and rapidly test them using laboratory-scale cell designs.



Increased renewables penetration on the grid

$$\textbf{Energy Density}_{RFB} \approx \tfrac{1}{2} nFV_{cell}c_{active}$$

$$ED_{AQ} = \tfrac{1}{2}1F1.5_{cell}2_{active} = \mathbf{1.5F}$$

$$ED_{IL} = \tfrac{1}{2}2F2_{cell}3_{active} = \mathbf{6.0F}$$

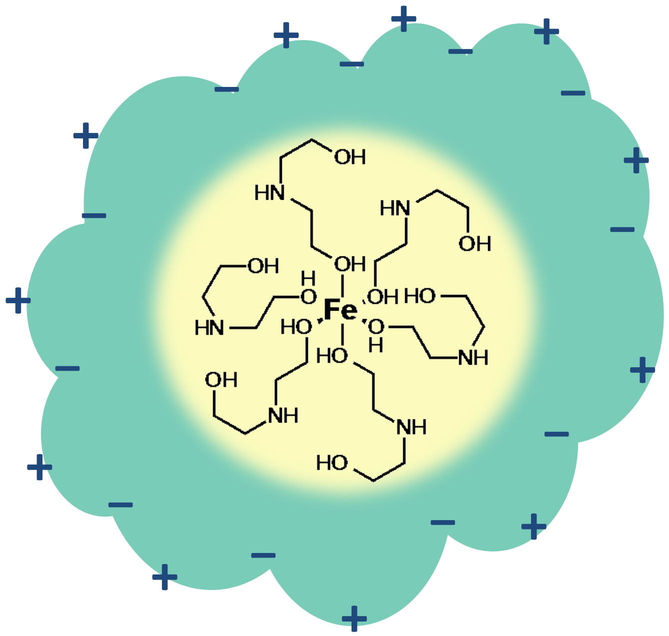
Potential for **four-fold** improvement

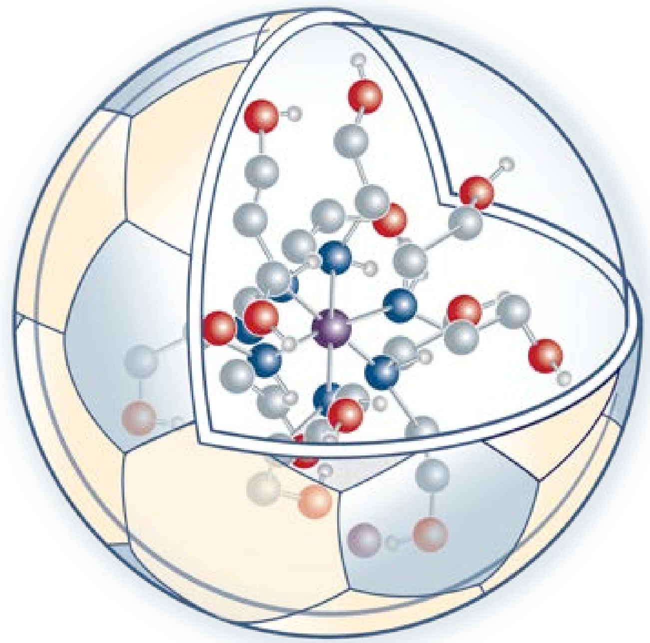
2015 Highlights:

- First ionic liquid RFB patent
- Membrane conductivity paper
- Significantly increased current densities

Pratt, Leonard, and Anderson, *EESAT* **2013**.

Metal Ionic Liquid (MetIL) Concept

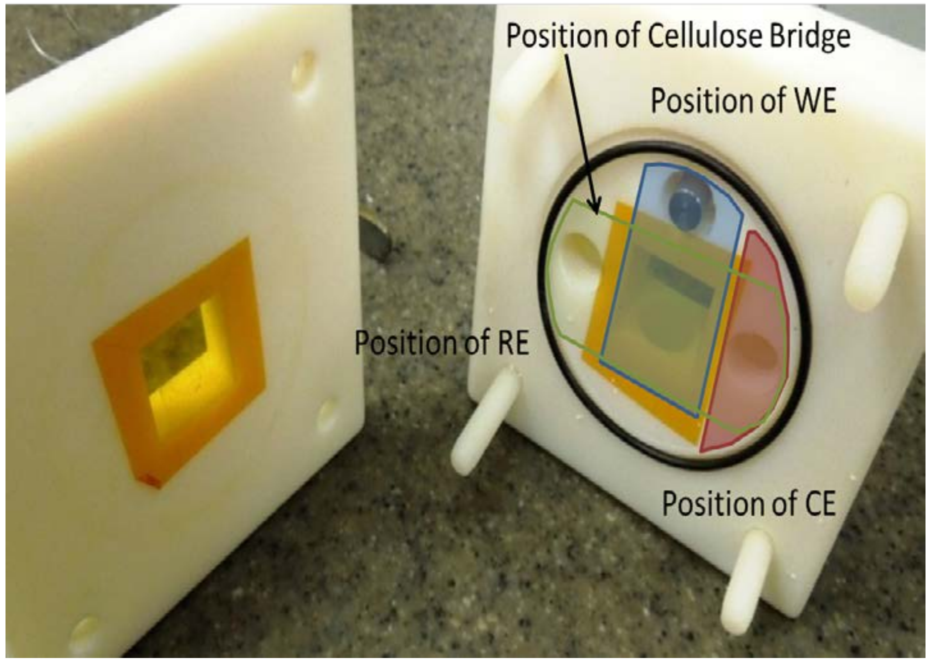




The "MetILs" Family

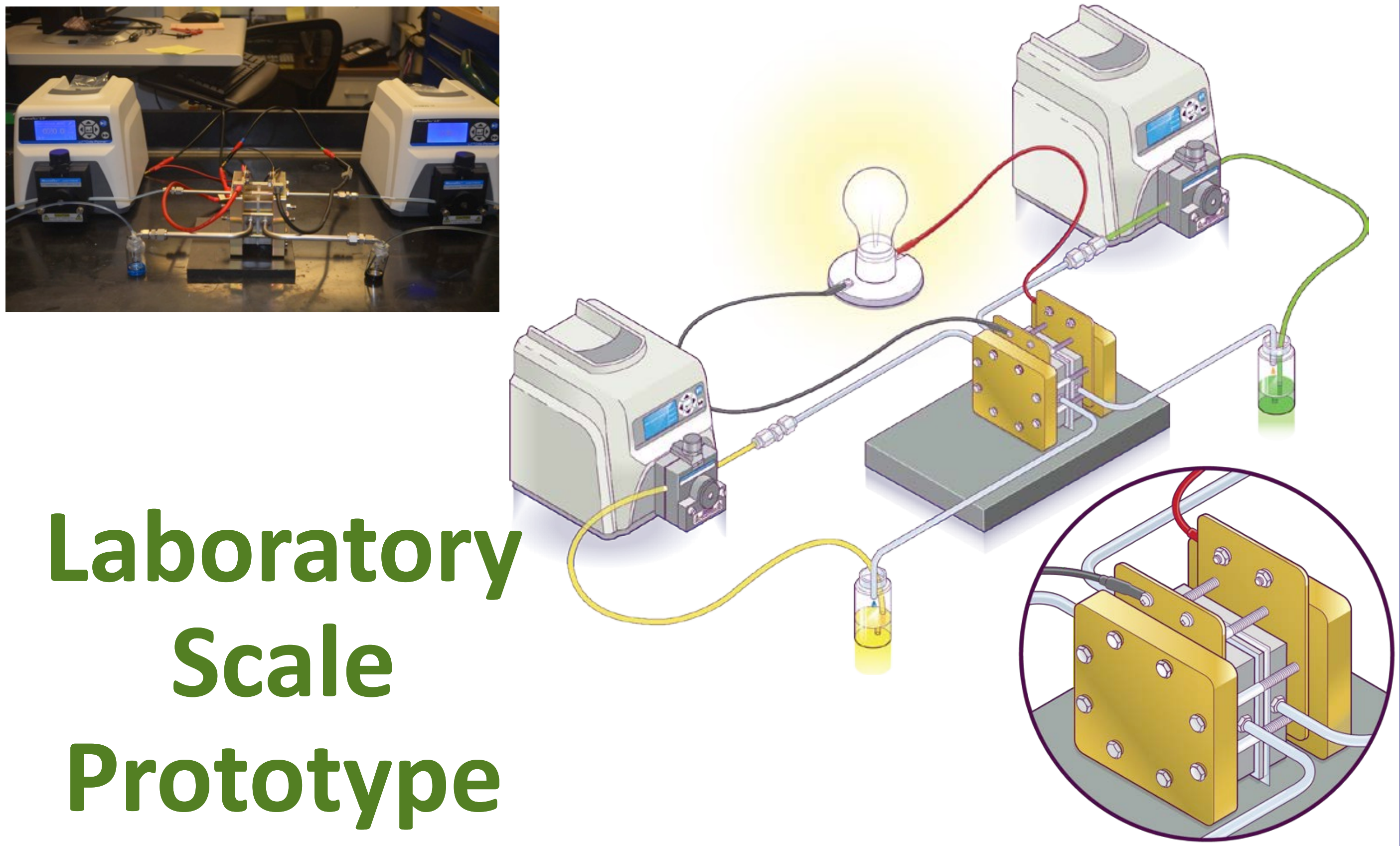
Approach: MetILs are synthesized in a single, high yield procedure using low cost, commercial precursors.

XANES/EXAFS[*]: *In situ* measurements show reduction of iron does not result in a decrease in iron-oxygen bond lengths, suggesting a significant shielding of the metal by the ligands from the external environment.



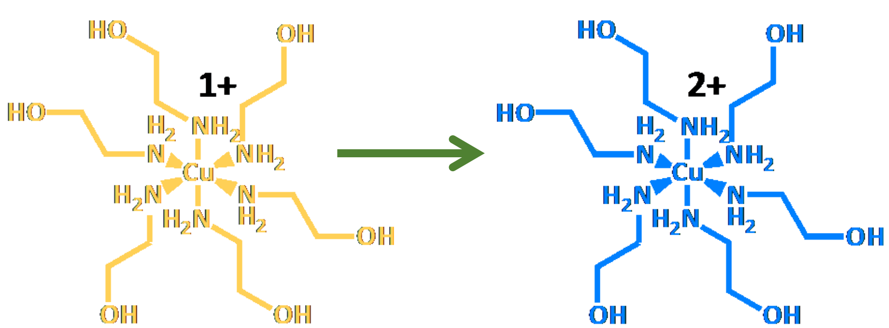
[*]Apblett et al., *Electrochim. Acta, submitted*.

Ionic Liquid Battery Prototype



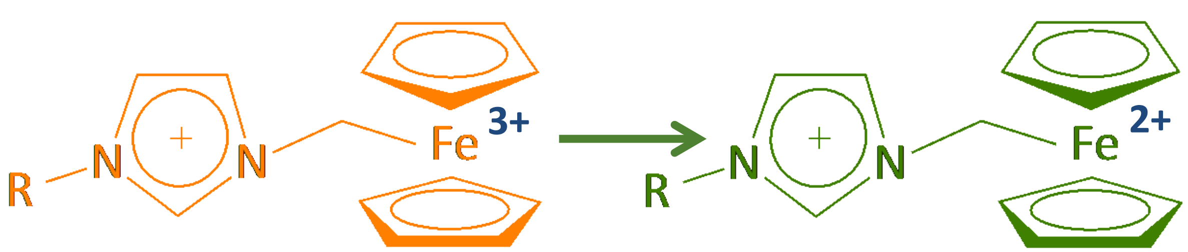
Laboratory Scale Prototype

- Initial tests on Cu-MetIL/Fe-MetIL system used commercial membranes.
- Neosepta AHA gave the best initial results for commercial membranes.
- Batteries were run at 50 ºC to improve the viscosity of the MetILs.



Negative Half-Cell Reaction

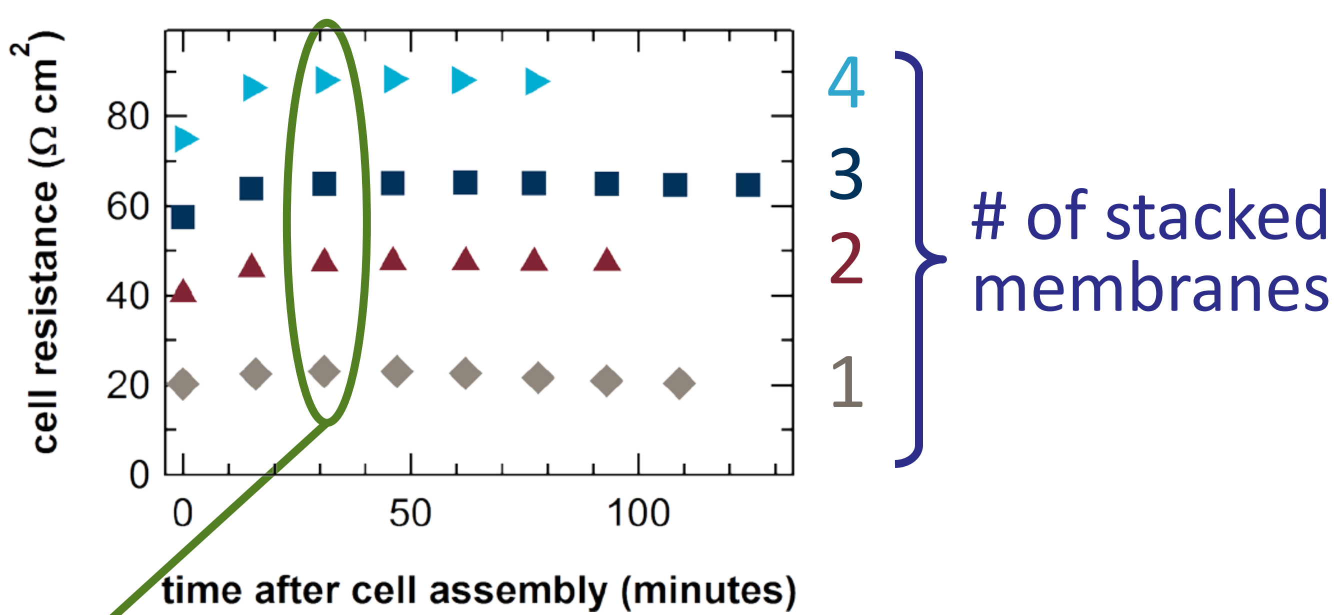
1.5 V

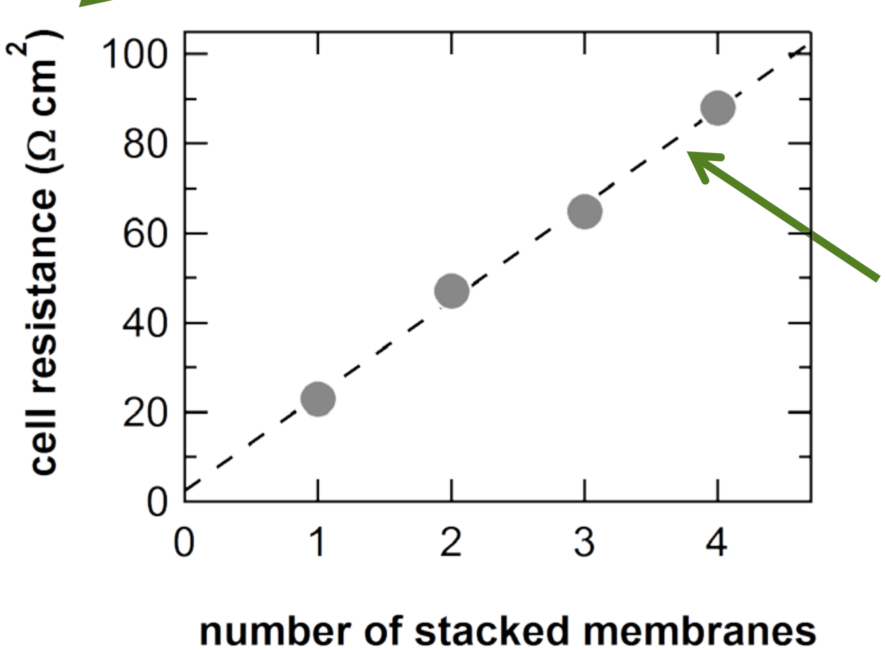


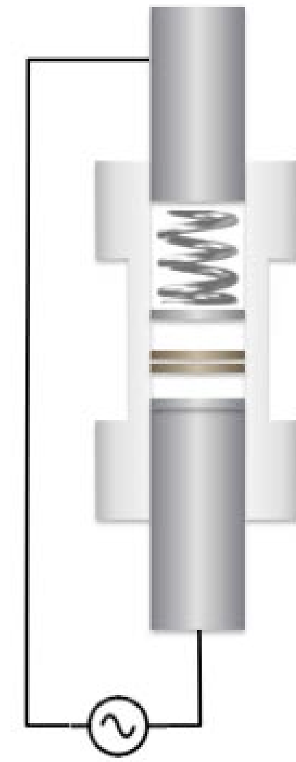
Positive Half-Cell Reaction

Highlight: First ionic liquid flow battery patent awarded in 2015

Membrane Through-Plane Resistance

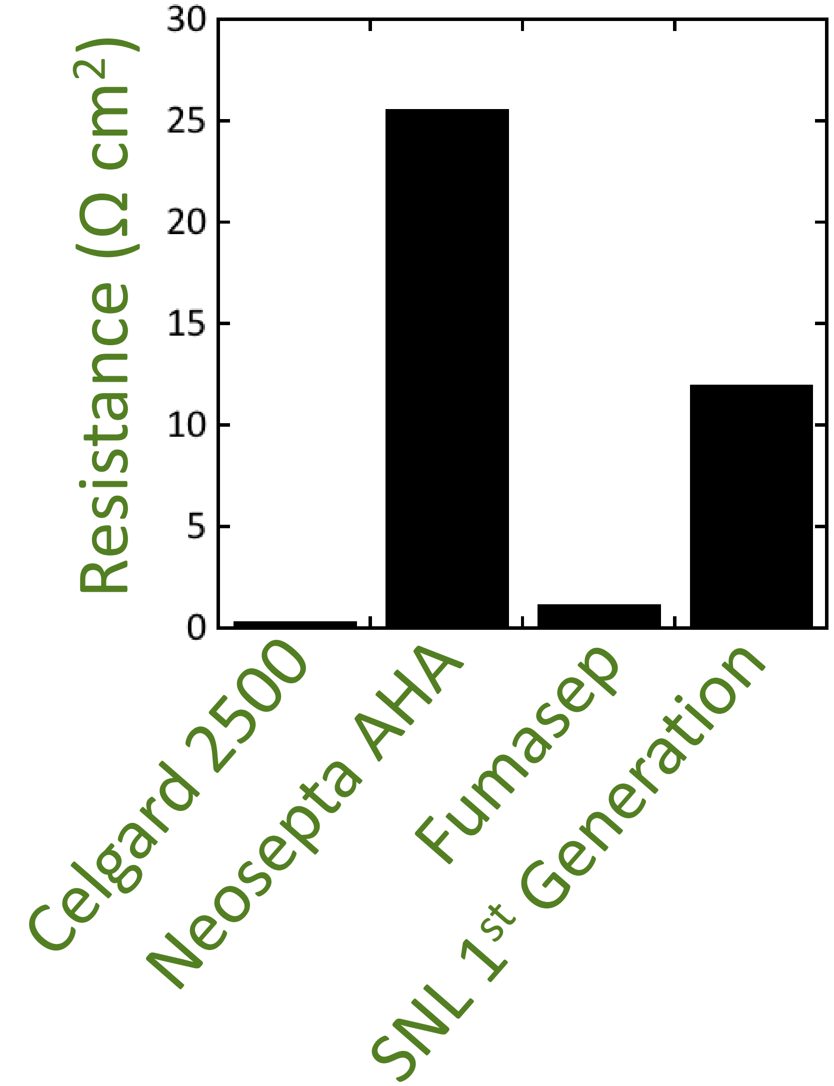






slope of fitted line =
21.3 $\Omega\ cm^2$
≡ area-specific resistance

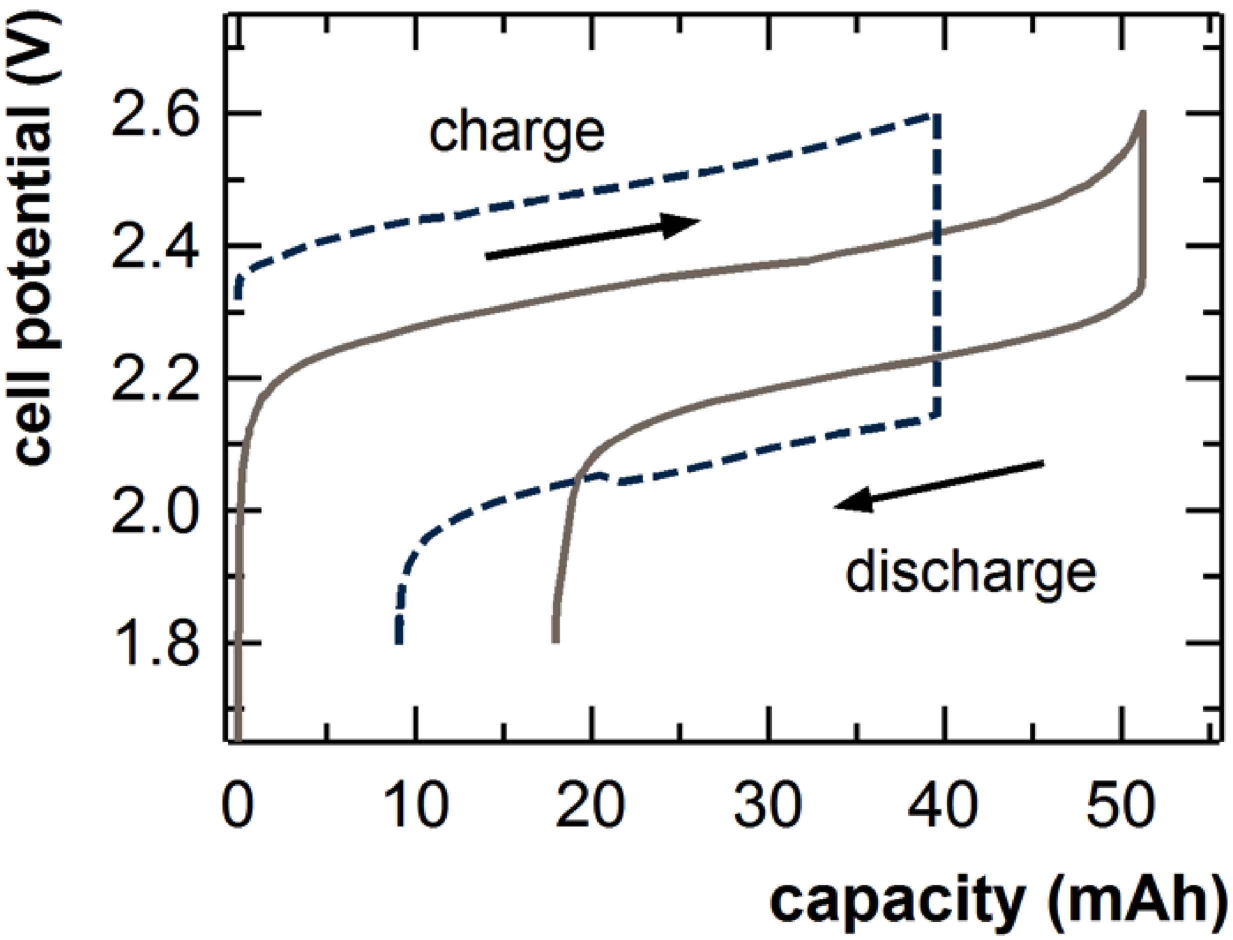
Membranes in 0.5 M $TEA\text{-}BF_4$/ACN

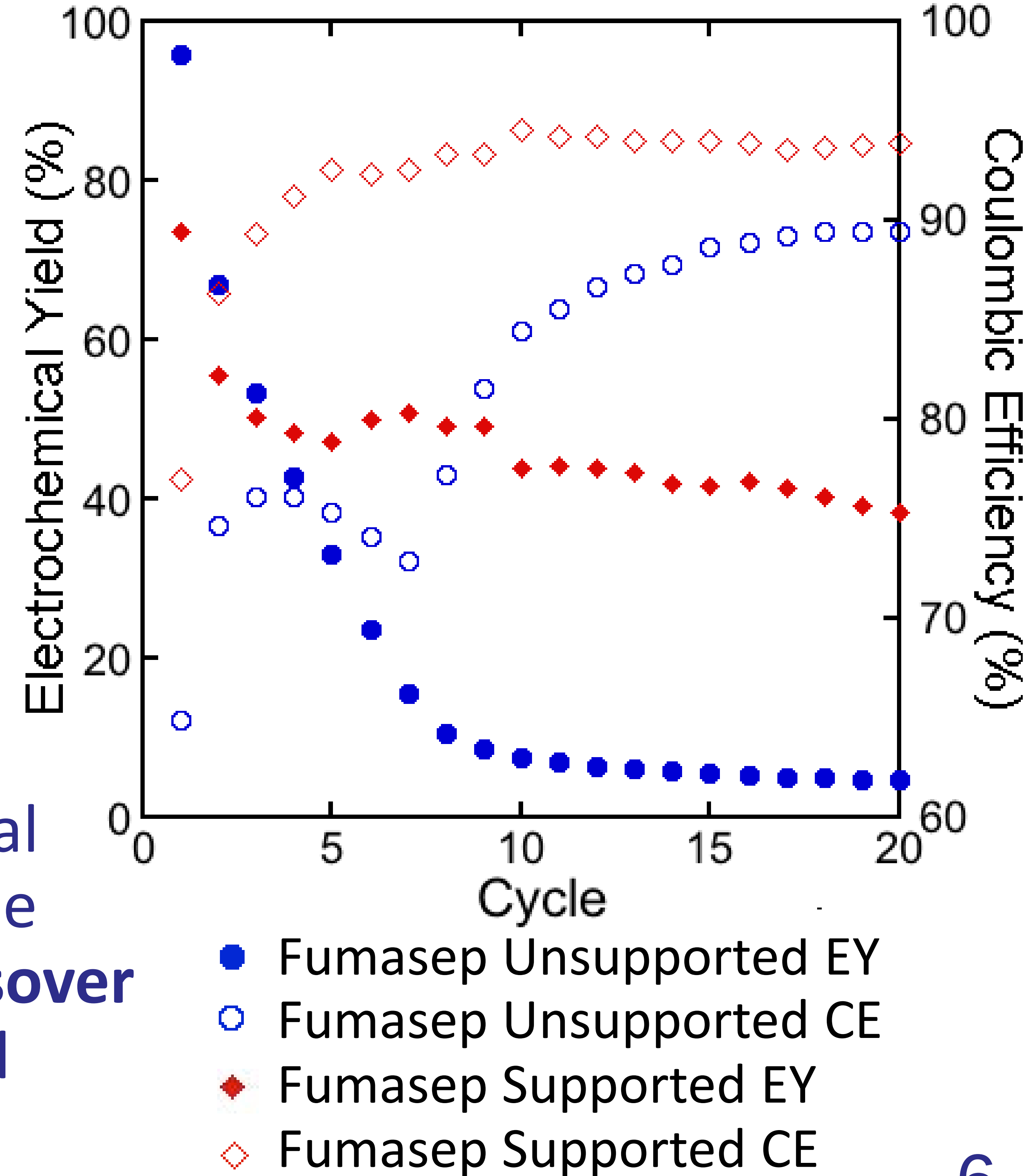


Different membranes in $TEA\text{-}BF_4$ illustrate a wide variability in resistances that in turn are solvent dependent.

Hudak, Small, Pratt, and Anderson, *J. Electrochem. Soc.* **2015**, p. A2188.

Flow Cell Studies



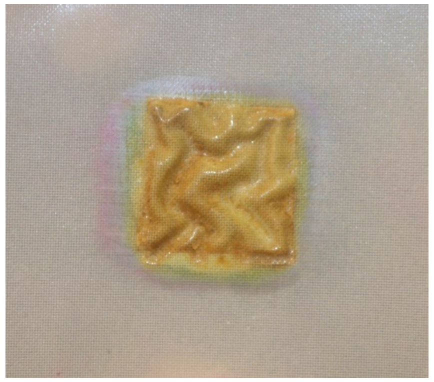
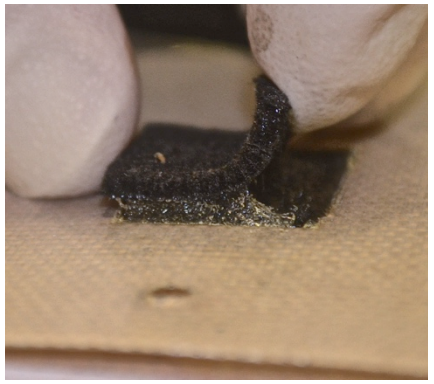
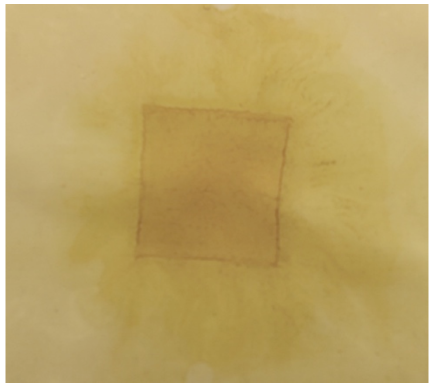


Highlight: The increased mechanical stability of the supported membrane suppressed **solvent-mediated crossover** and enabled higher electrochemical yields and Coulombic efficiencies.

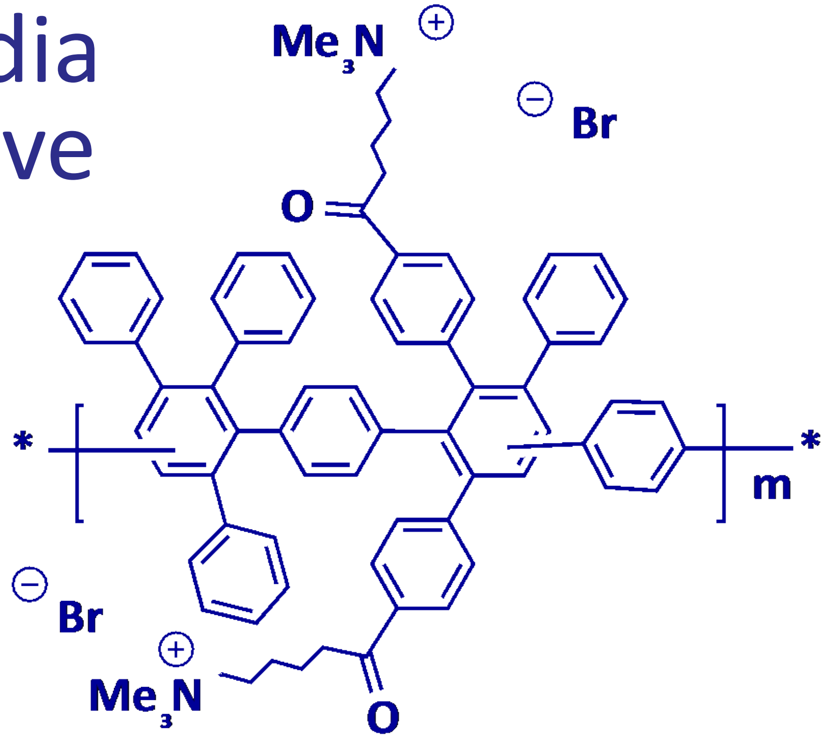
Hudak, Small, Pratt, and Anderson, *J. Electrochem. Soc.* **2015**, p. A2188.

Membranes

Most commercially available, ion selective membranes are not designed for non-aqueous use.

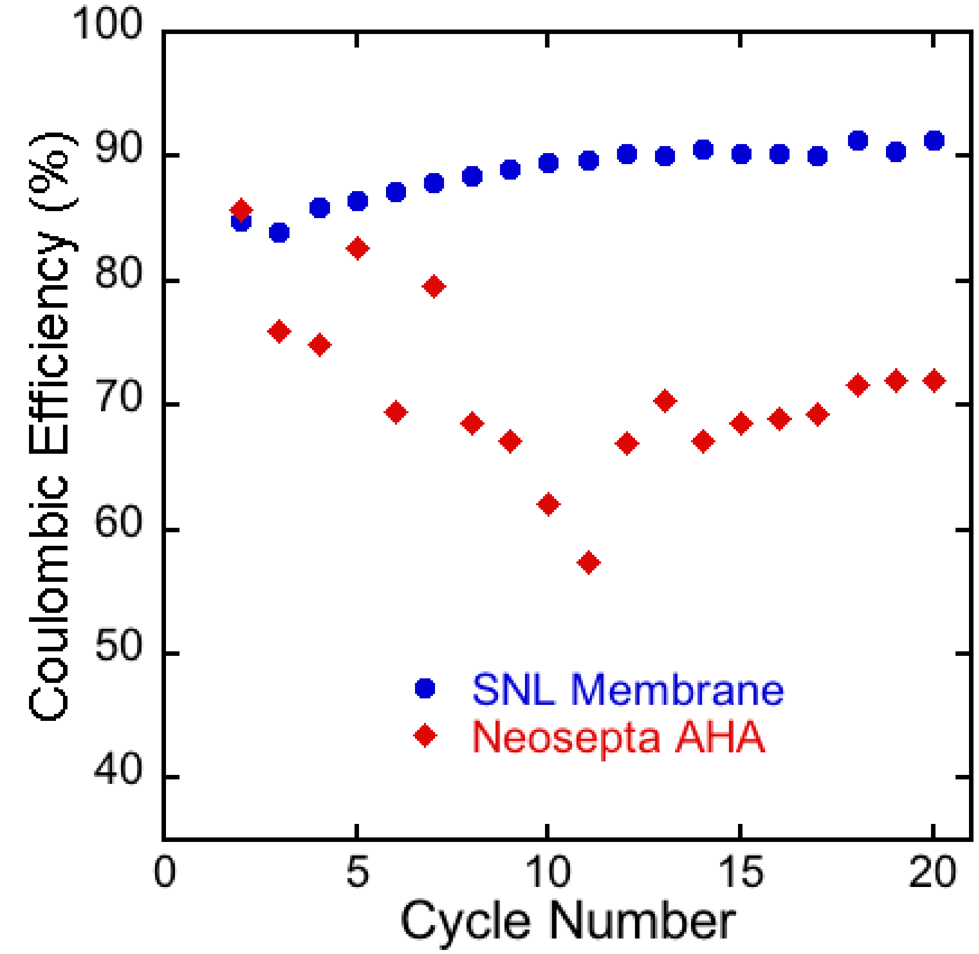
Commercial	1st Generation SNL*	2nd Generation SNL*
		

Highlight: Sandia membranes have increased chemical and temperature stability over commercial materials.



1st Generation Results:

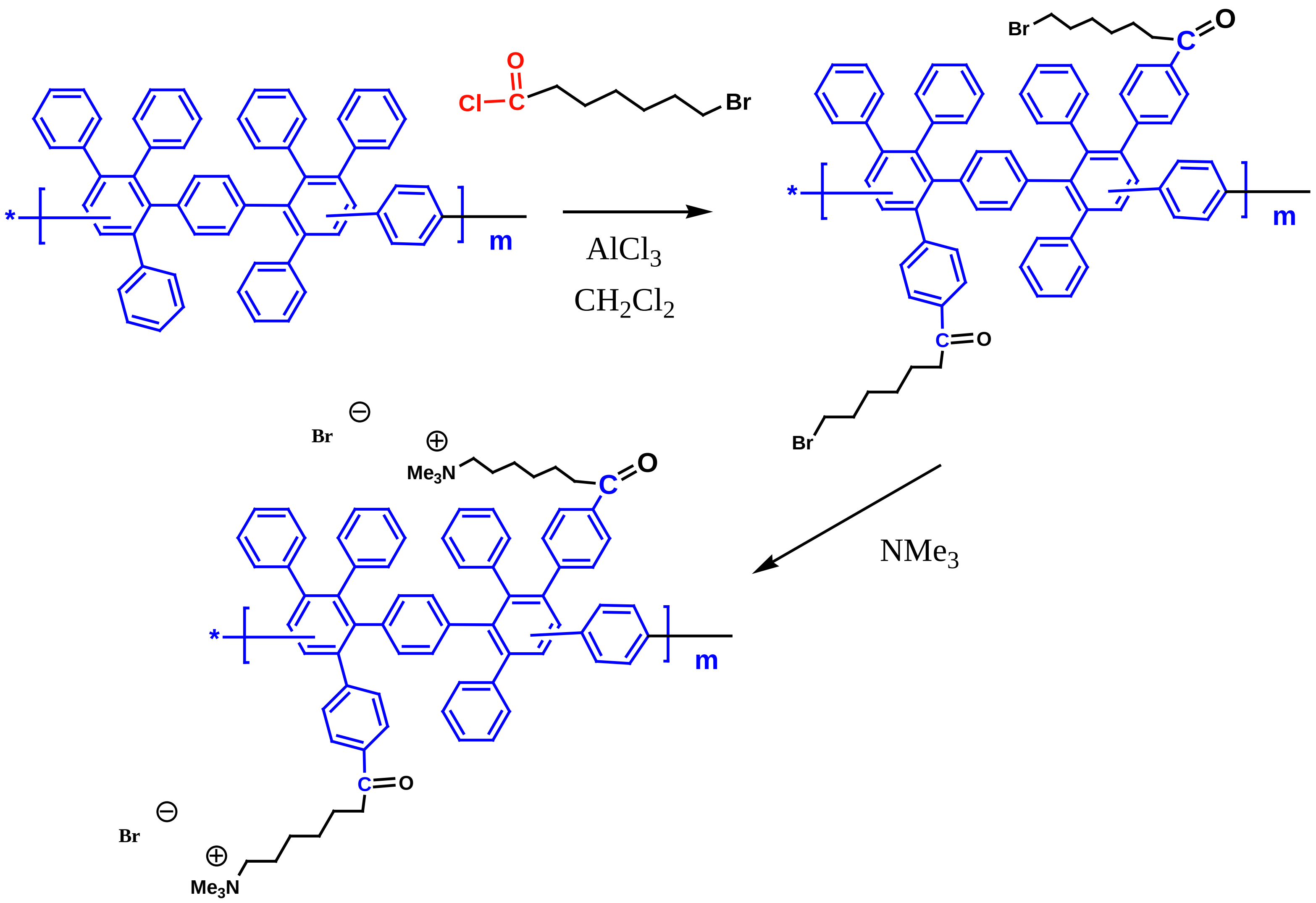
- Coulombic efficiency increased from 70% to 90%.
- Current density increased from 0.5 to 10 mA/cm^2.



*Cy Fujimoto

Membrane Ion Content

Membranes contain a polyphenylene backbone with pendant ionic groups; ionic content was varied qualitatively high, medium, and low.



Low Ion Content

Very brittle sample–no data

Medium Ion Content

Best Coulombic efficiency

Best electrochemical yield

Least crossover

High Ion Content

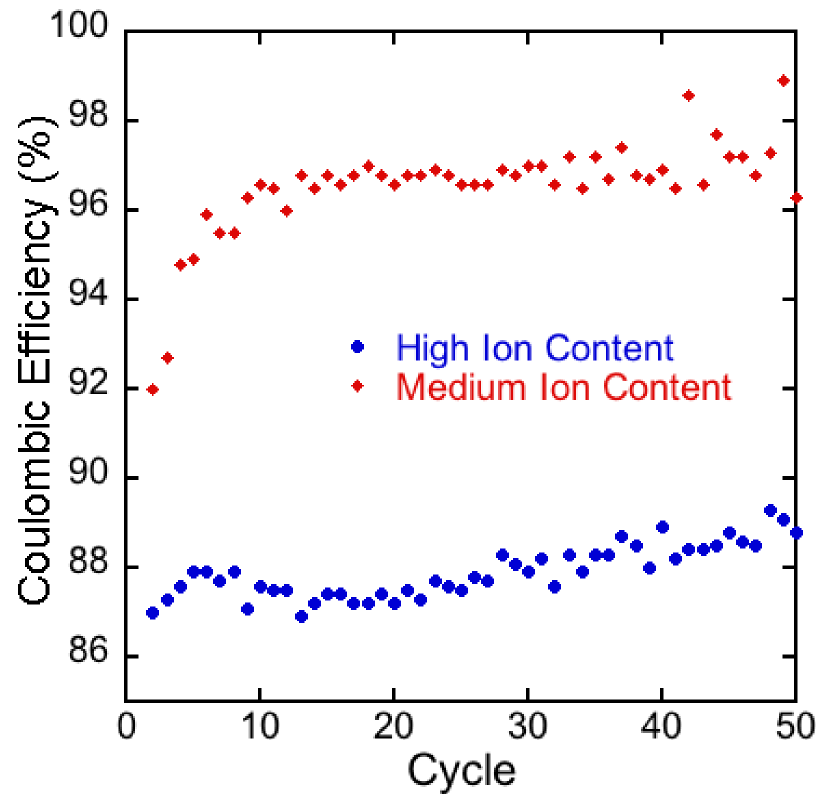
Good Coulombic efficiency

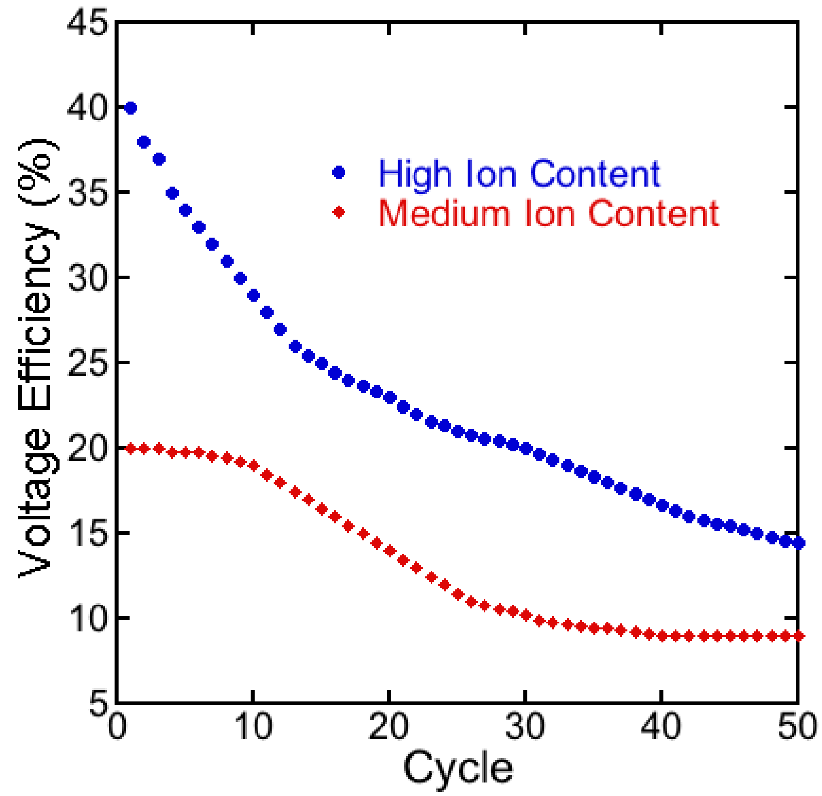
High crossover

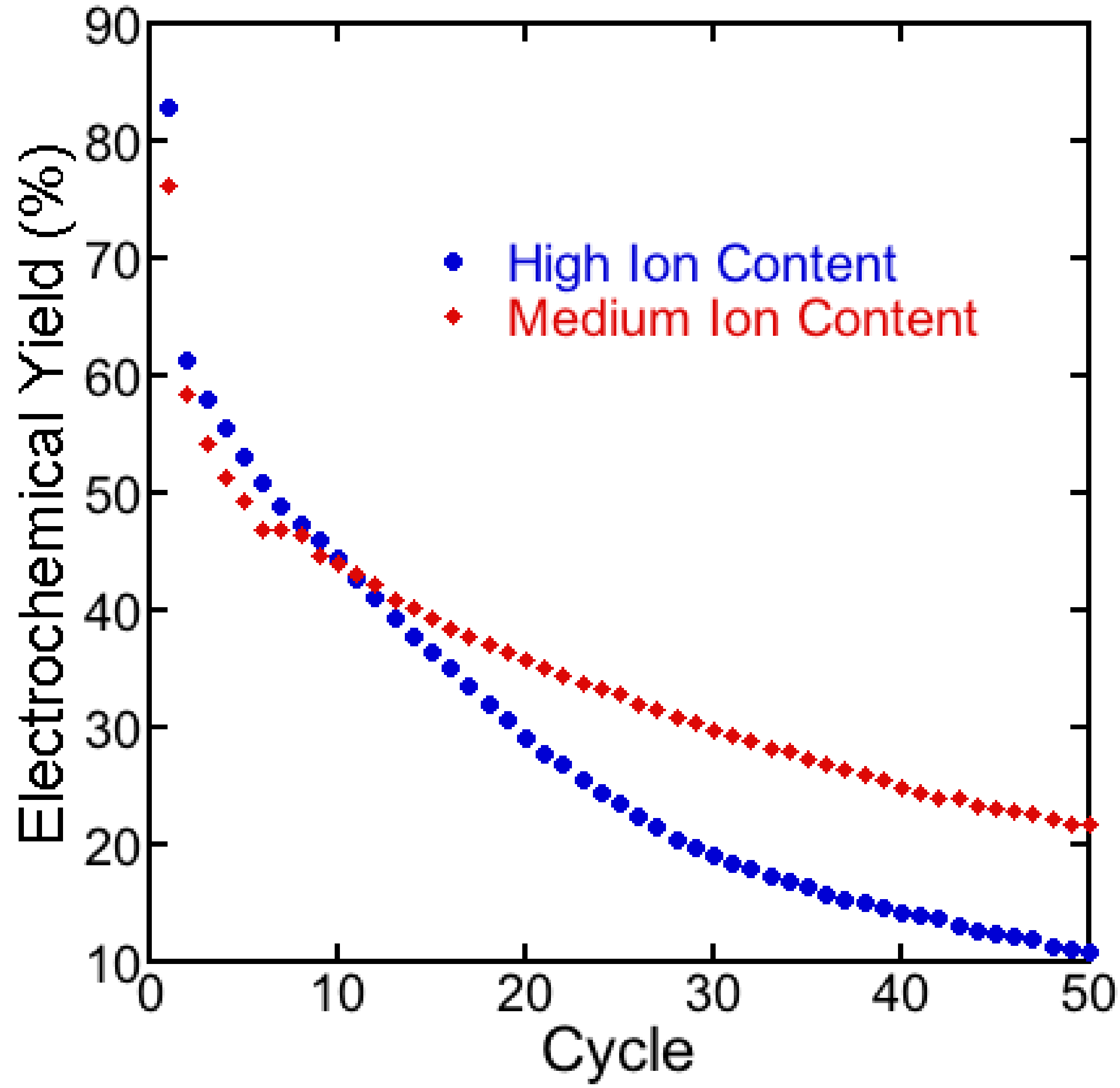
The membranes are prepared by a propriety process using Friedel Crafts acylation with a ketone to add pendant ammonium groups and simultaneously lightly crosslink the polymer backbone.

Small, Pratt, Fujimoto, and Anderson, *J. Electrochem. Soc.*, in submission.

Cell Cycling High/Medium Ion Content



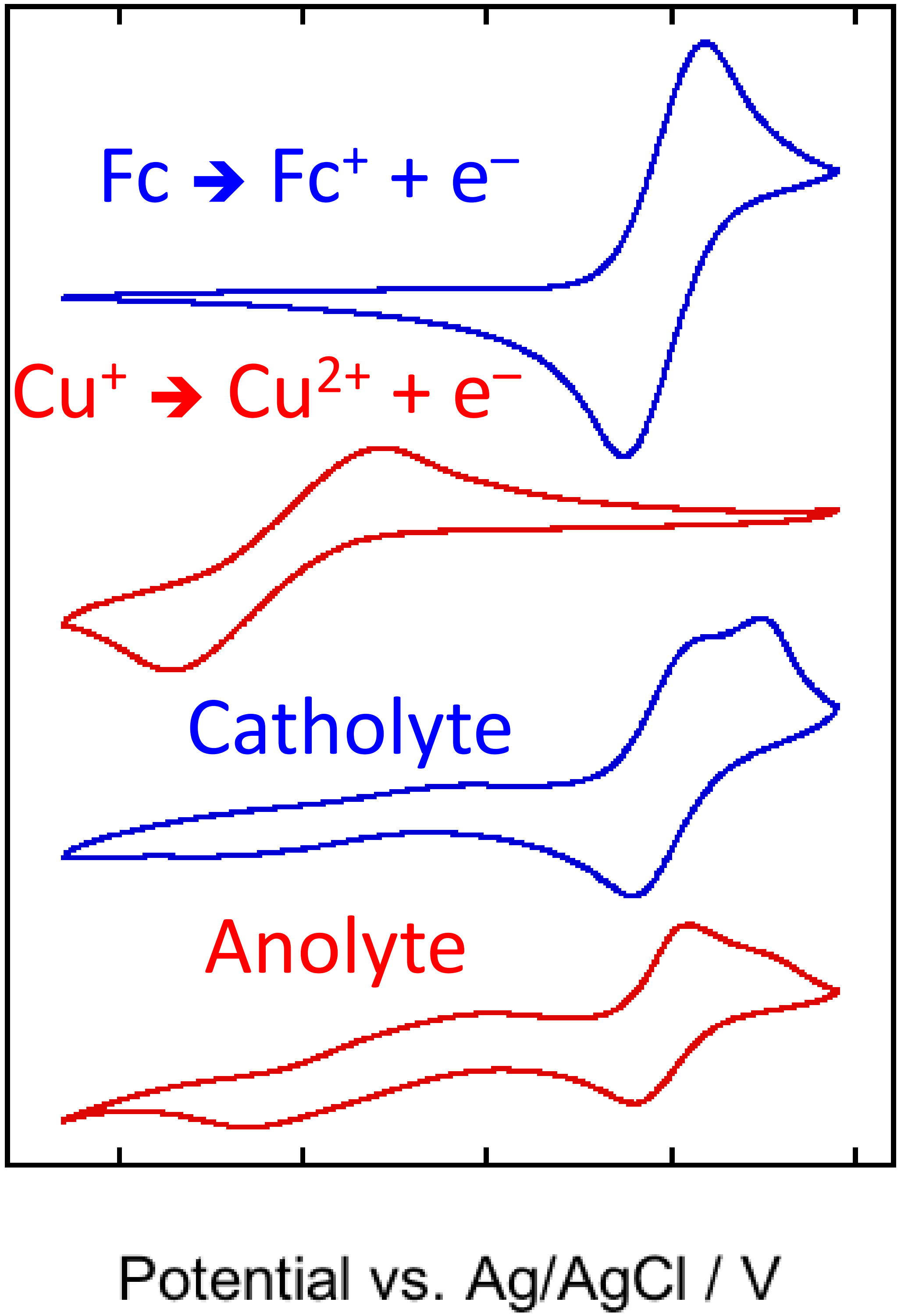


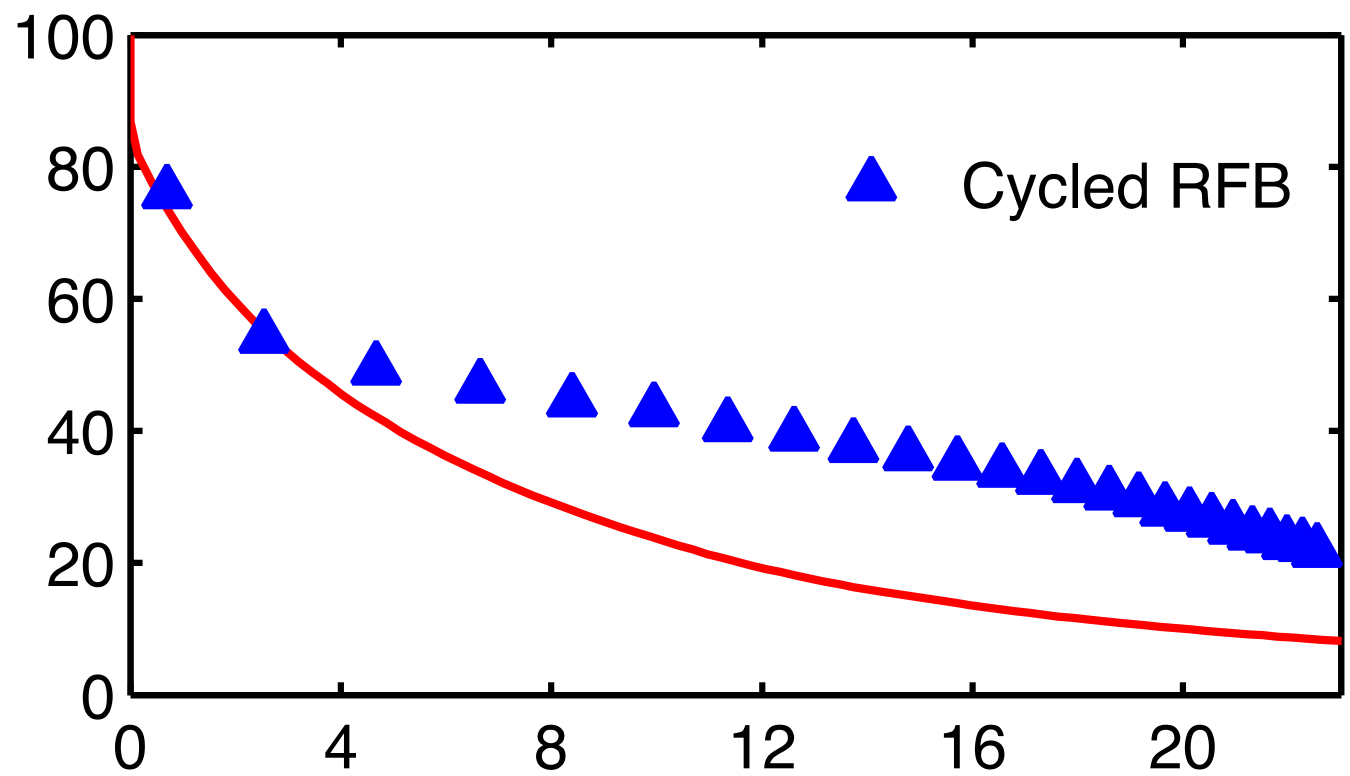


The decreased electrochemical yield was investigated by (1) **cycling rate effects**; (2) **crossover measurements**; (3) **impedance**; (4) **membrane stability**.

Small, Pratt, Fujimoto, and Anderson, *J. Electrochem. Soc.*, in submission.

Post Cycling Studies





- Theoretical electrochemical yield for a static cell was determined from the OCP and the Nernst equation.
- The overlay of the static and cycled data show that crossover was responsible for the lowered electrochemical yield.

Small, Pratt, Fujimoto, and Anderson, *J. Electrochem. Soc.*, in submission.

Summary/Conclusions

Metallic ionic liquids address:

- **Energy density** through higher metal concentrations and wider voltage windows
- **Life cycle costs** through earth abundant materials
- **Round trip efficiency** through high electrochemical reversibility and conductive membranes
- **Cycle life** through chemically stable materials

FY15 Accomplishments:

- Developed new polyphenylene membranes with 20% increase in Coulombic efficiency and 30% increase in electrochemical yield
- As of FY15, published 12 articles, 15 conference papers, two journal covers, and submitted 4 patents (one awarded)

FY16 Plans:

- Move toward a more viable system through–
  - Addressing **capacity fade** through tunable membranes chemistries
  - Further increasing cell voltages through new lead and cobalt electrolytes

Thank you to the DOE OE and especially Dr. Imre Gyuk for his dedication and support to the ES industry and Sandia's ES Program.

Questions?

Principal Investigator Contact Information:
Travis Anderson
Sandia National Laboratories
PO Box 5800
Albuquerque, NM 87185-0613
tmander@sandia.gov